REPORT DOCUMENTATION P

oved
0704-0188

(2)

AD-A236 882

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b.
2a. SECURITY CLASSIFICATION AUTHORITY	3. Distribution unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Advanced Technology Materials Inc.	6b. OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code): 7 Commerce Drive, Danbury, CT 06810	7b. ADDRESS (City, State, and ZIP Code): Department of the Navy, 800 N. Quincy Street, Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-90-C-0201	
8c. ADDRESS (City, State, and ZIP Code): Department of the Navy, 800 N. Quincy Street, Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
MOCVD of TlBaCACuO: Structure Property Relations and Progress Towards Device Processing

12. PERSONAL AUTHOR(S)
Norihito Hamaguchi, Robin A. Gardiner and Peter S. Kirlin

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	May 31, 1991	13

16. SUPPLEMENTARY NOTATION

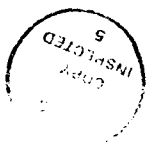
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Highly c-axis oriented $Tl_2Ba_2CaCu_2O_x$ thin films were grown on MgO(100) by MOCVD and post annealing processes. Resistive transitions ($R \leq 0.1$ μΩ-cm) of 105 K, critical current densities as high as 10^5 Amps/cm^2 (4 K) and surface resistivities 1/2 to 1/5 that of a gold standard at 17 GHz (77 K) were obtained with unpatterned films. Thin (0.1 μm) TlBaCaCuO films functioned as bolometric detectors over a spectral range of 1.5 to 20 μm; no quantum or nonequilibrium effects were observed between 4 and 125 K. Fine features were delineated in the BaCaCuO thin films by wet chemical etching. After Tl incorporation, resistive transitions exceeding 103 K were observed in the patterned films.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: Daniel P. Sharkey	22b. TELEPHONE (Include Area Code): 203-749-1100 / 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete — SECURITY CLASSIFICATION OF THIS PAGE



OFFICE OF NAVAL RESEARCH

Office of Naval Research

Contract N00014-90-C-0201

R&T Code htsc001

Technical Report No. 2

MOCVD of TlBaCACuO: Structure Property Relations and Progress towards Device Processing

by

Norihito Hamaguchi, Robin A. Gardiner and Peter S. Kirlin

Prepared for Publication

in the

Proceedings of the SPIE '90

Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810

May 31, 1991

1394-26

MOCVD of TlBaCaCuO: structure-property relations and progress toward device applications

N. Hamaguchi, R. Gardiner, P. S. Kirlin

Advanced Technology Materials, Inc., 520-B Danbury Rd., New Milford, CT 06776

ABSTRACT

Highly c-axis oriented $Tl_2Ba_2CaCu_2O_x$ thin films were grown on MgO(100) by MOCVD and post annealing processes. Resistive transitions ($R \leq 0.1$ μΩ-cm) of 105 K, critical current densities as high as 10^5 Amps/cm^2 (4 K) and surface resistivities 1/2 to 1/5 that of a gold standard at 17 GHz (77 K) were obtained with unpatterned films. Thin (0.1 μm) TlBaCaCuO films functioned as bolometric detectors over a spectral range of 1.5 to 20 μm; no quantum or nonequilibrium effects were observed between 4 and 125 K. Fine features were delineated in the BaCaCuO thin films by wet chemical etching. After Tl incorporation, resistive transitions exceeding 103 K were observed in the patterned films.

1. INTRODUCTION

The quality of high temperature superconducting thin films has improved to the point where the fabrication of a limited range of devices with respectable performance is possible. In particular, dc SQUIDs with noise levels comparable to commercial low T_c rf SQUIDs[1] and passive microwave components with losses 10 times lower than that of equivalent Cu devices at 77 K and 3.29 GHz[2] have been fabricated from TlBaCaCuO thin films. Different applications, eg. IR detectors versus microwave filters, may require different properties. Current efforts are focused on establishing structure-property-device performance relationships and on optimizing the HTSC thin film deposition and processing protocols for a given application. In general the basic chemical, mechanical and physical properties of the films are different for each individual deposition method and/or application and tailored patterning/etching, metallization, passivation, packaging, and post-annealing (if required) protocols must be developed to optimize a specific type of devices' reproducibility and performance. Reported below are recent results from our laboratories on the preparation of TlBaCaCuO thin films on MgO(100) by MOCVD and post annealing and the fabrication of passive microwave components and infrared detectors by variants of standard semiconductor processing methods.

2. PREPARATION AND CHARACTERIZATION

2.1 MOCVD of BaCaCuOF

BaCaCuOF thin films were deposited on MgO(100) single crystal substrates by MOCVD. The source reagents used for the deposition of the precursor films were barium and calcium 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate

($Ba(fod)_2$ and $Ca(fod)_2$) and copper hexafluoroacetylacetonate. The MOCVD experiments were carried out in an inverted vertical reactor designed to achieve stagnation point flow and growth rates approaching 0.4 μm/hr were achieved at a susceptor temperature of 500°C and a reactor pressure of 4 torr. Typical run conditions are listed in Table 1; a more detailed description of the reactor system[3] and growth tube[4] are reported elsewhere.

TABLE 1. Deposition conditions for BaCaCuOF films.

O_2 flow rate (sccm)	Ar flow rate (sccm)	Source reagent transport rate (10^{-6}mole/m) $Ba(fod)_2$	$Ca(fod)_2$	$Cu(hfacac)_2$
170	190 ~210	12 ~ 18	6 ~ 15	0.35 ~ 0.56

2.2 Annealing

The as-deposited films were amorphous mixtures of oxides and fluorides as determined by x-ray diffraction (XRD) and energy dispersive x-ray (EDX) analysis.[5] This result agrees well with that observed for the MOCVD of BiSrCaCuOF using similar source reagents and deposition conditions.[4] The fluorine was removed in flowing wet oxygen at 785°C and the morphology of the films changed from highly porous to uniform densely packed grains. Tl was then incorporated into the BaCaCuO films at 870°C. The precursor films were placed face down between two stoichiometric $Tl_2Ba_2Ca_2Cu_3O_x$ pellets and loaded into a capped alumina boat. The alumina boat was placed inside a standard tube furnace and heated to 870°C at 100°C/min. The pellets were the source of Tl_xO_y vapor and they were prepared by mixing Tl_2O_3 and BaCaCuO powder in a Tl:Ba:Ca:Cu molar ratio of 2:2:2:3 followed by static pressing at 1 x 10^8 Pa. Ideally, this strategy provided a Tl_xO_y partial pressure above the BaCaCuO precursor film equivalent to that over stoichiometric $Ba_2Ca_2Cu_3O_x$ powder. Whether or not this situation was achieved is unclear; however, adhering to this combination of pellet stoichiometry and oven configuration was crucial to reproducibly obtaining complete thallium uptake during the second annealing step.

The structural properties of the films were evaluated with XRD and SEM. Typical surface morphologies of the films annealed at 870°C consisted of platelet-like grains 5 to 10 μm in diameter and XRD indicated that the films were c-axis oriented and that $Tl_2Ba_2CaCu_2O_8$ was the only crystalline phase present.[5,6] Standard four point probe (Figure 1), rf eddy current (Figure 2), and dc susceptibility (Figure 3) measurements indicate that a percolative path becomes fully superconducting at 105 K and that intra- and/or inter-grannular coupling

occurs all the way down to 4 K. The transition in the rf eddy current measurement is complete by ca. 70 K which supports the latter interpretation and the strong suppression of the critical current density by a 800 Oe magnetic field applied parallel to the surface of the film but perpendicular to the direction of the current flow strongly suggests that the films are weakly linked.[5] The transport critical current density (J_c) of the films was measured to be 10^5 Amps/cm^2 at 4.2 K using the 1 μV/cm criterion. The surface resistance (R_s) of the TlBaCaCuO films was measured in a parallel plate cavity resonator and the R_s of the best unpatterned films was approximately 1/2 to 1/5 that of Au standard at 77 K and 17.3 GHz.[5]

Figure 1. Resistive transition of $Tl_2Ba_2CaCu_2O_x$/MgO(100)

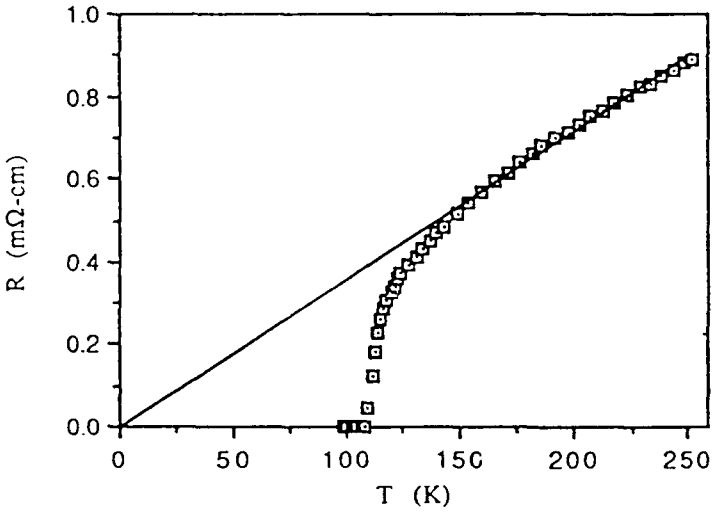


Figure 2. Inductive transition of $Tl_2Ba_2CaCu_2O_x$/MgO(100)

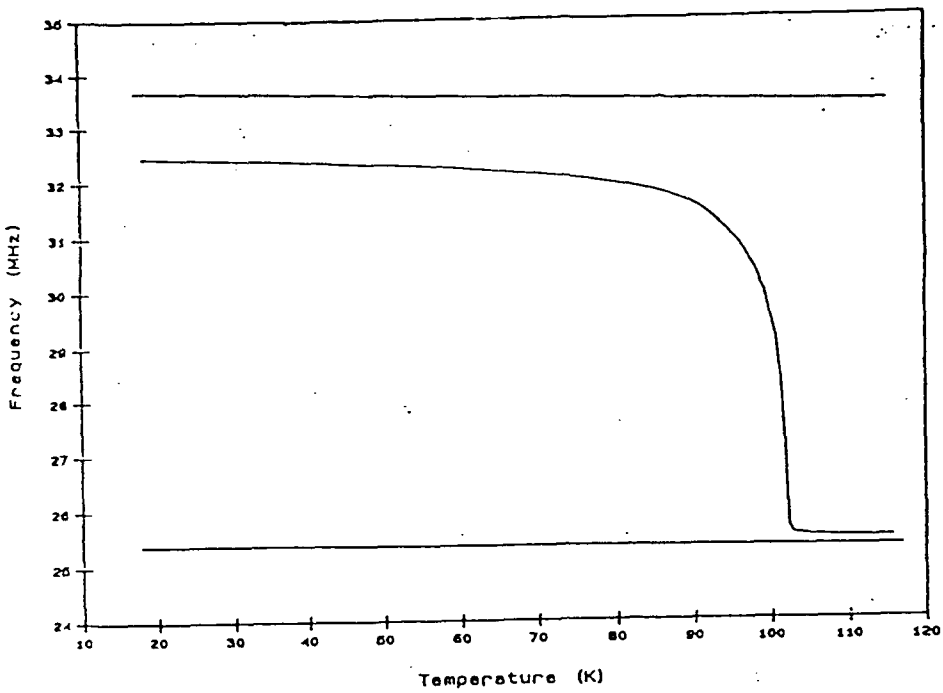
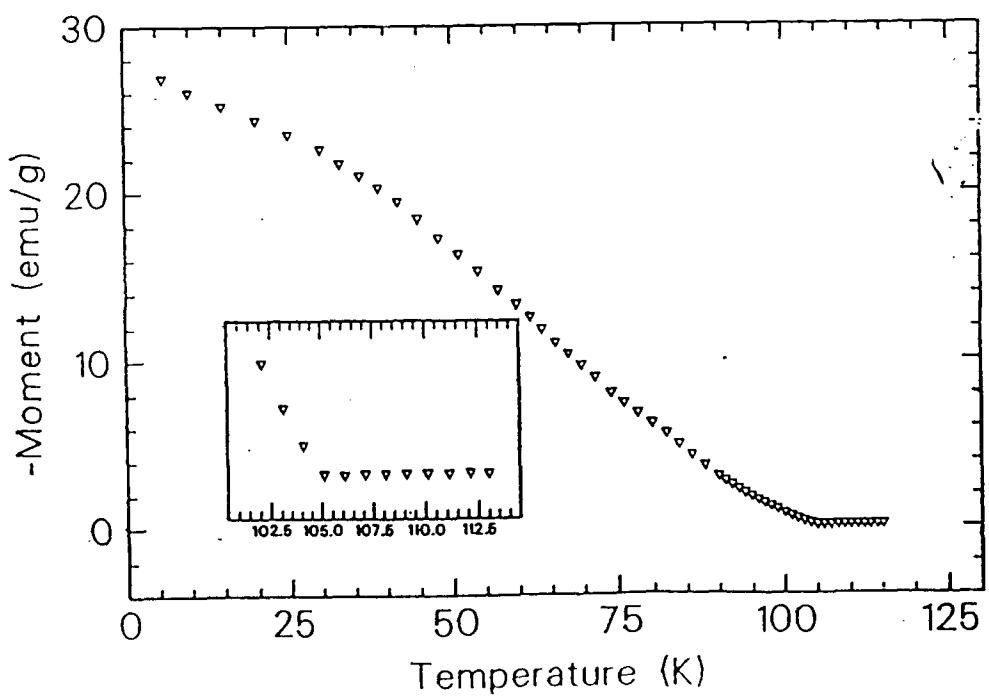


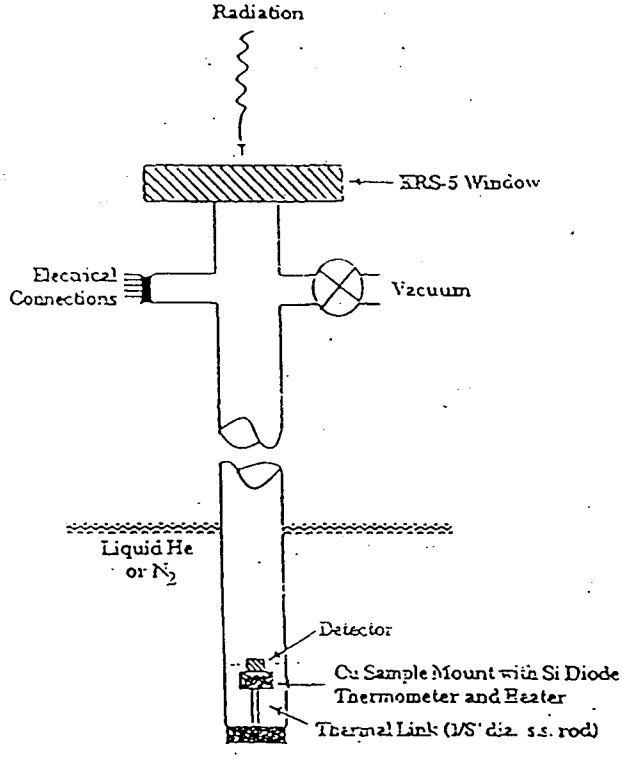
Figure 3. Meissner effect data measured by cooling in a 5 Oe magnetic field applied normal to the surface of the $Tl_2Ba_2CaCu_2O_x$ film



2.3 Infrared Response

The infrared response of the TlBaCaCuO thin films over a spectral band of 1.5 to 20 μm was measured with a calibrated glowbar source (1250±10 K) in a liquid helium cooled cryostat. The incident radiation was chopped at 15 Hz by a mechanical chopper and the power at the sample was approximately 25 μW. A schematic of the measurement system is shown in Figure 4; a more detailed description of the measurement apparatus can be found elsewhere.[7]

Figure 4. Rapid change cryostat for evaluating IR response



The infrared response measurements were made on TlBaCaCuO films whose thickness (≤0.1 μm) was comparable to the optical penetration depth to ensure that the infrared radiation sampled the entire film volume. Consequently, complications arising from shunting effects, which have been encountered with bulk and standard thin film samples, should have been minimal. In addition to the TlBaCaCuO films, low quality YBaCuO films were characterized with the hope of observing a nonequilibrium response. The optical detection in the TlBaCaCuO and YBaCuO thin films was investigated between 4.2 and 130 K and all the samples functioned as standard bolometric detectors at the

superconducting to normal transition. Only a single YBaCuO sample which never became fully superconducting (Figure 5) exhibited a response at 4.2K which deviated from dR/dT. The thermal detection coefficients of the TlBaCaCuO/MgO(100) samples were calculated from the resistive transition curves and the shape of the measured response curves typically agreed well with that expected on theoretical grounds (Figure 6). No evidence for quantum or nonequilibrium effects was observed for the TlBaCaCuO films in this temperature range.

Figure 5. Resistive transition of YBaCuO/MgO(100)

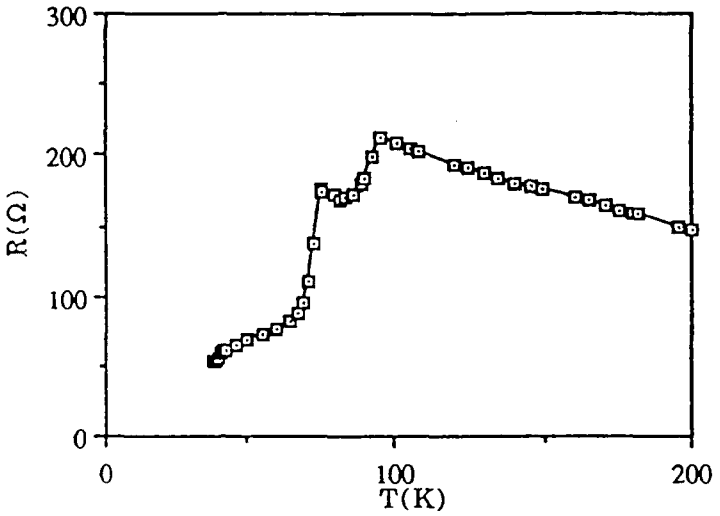
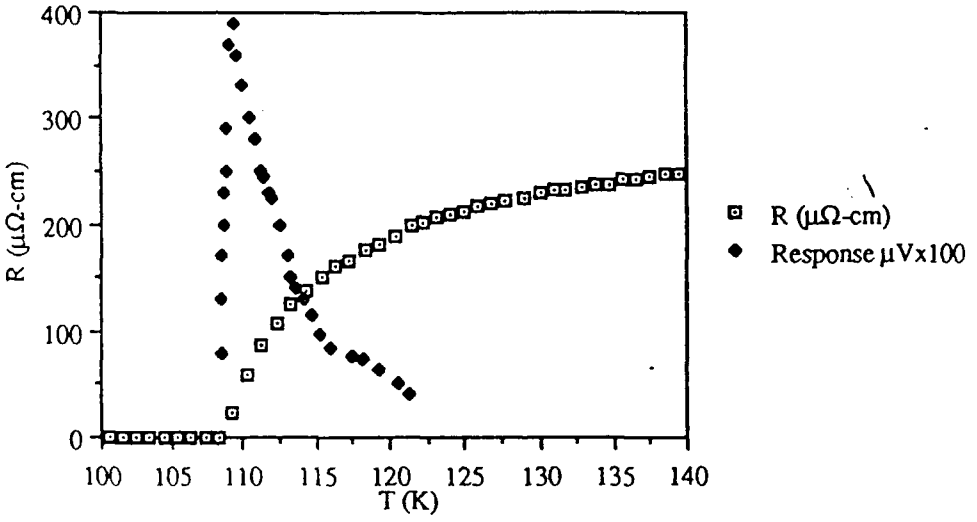
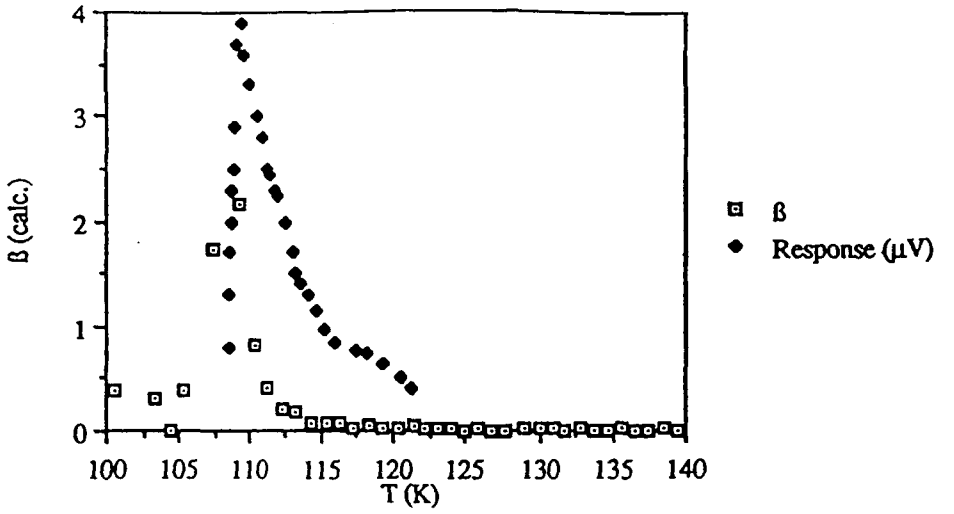


Figure 6 IR response of TlBaCaCuO/MgO(100) compared to the (a) resistivity and (b) calculated thermal detection coefficient



(a)



(b)

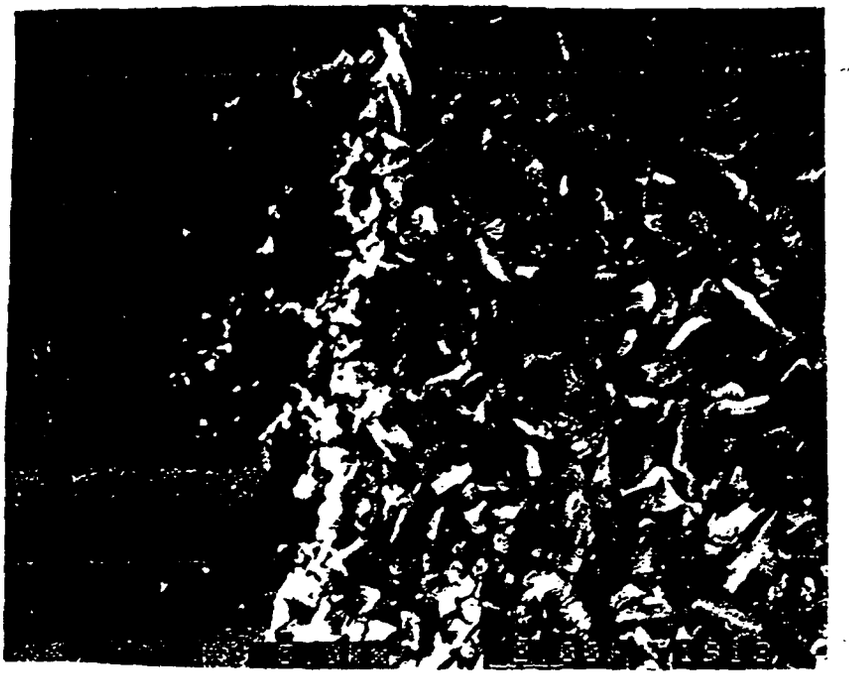
3. DEVICE FABRICATION

Electronic applications require the delineation of fine features in the HTSC thin films. Aqueous-based wet chemical processing technology which is widely used in the semiconductor industry, particularly in the manufacture of microwave components, potentially could provide an economically viable means of fabricating large numbers of HTSC devices. However, aqueous based processing has been shown to be detrimental to the properties of HTSC thin films.[8,9] This limitation can be overcome by patterning and etching the BaCaCuO thin films before Tl incorporation. This approach has the added advantage of not generating aqueous Tl containing waste and if appropriately optimized the high temperature Tl incorporation step can present surfaces whose stoichiometries approach that of the bulk.

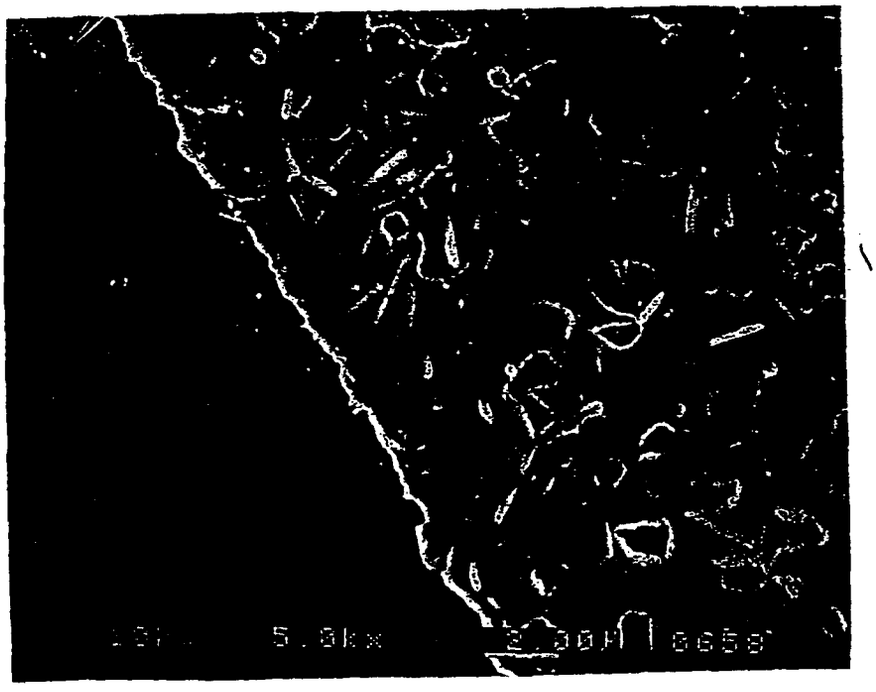
The BaCaCuO films were patterned with positive photoresist and etched with a dilute HCl/DI water solution (1/200); typical etch rates were 1.2 μm/min. The resist mask was removed using acetone followed by oxygen plasma ashing. The protected areas of the BaCaCuO films remained largely intact during the patterning and only a minimal amount of deterioration occurred along the edges of the patterned features (Figure 7a). The quality of the edges consistently improved during the Tl incorporation step which was carried out at a maximum temperature of 850°C (Figure 7b) and the average film density was typically superior to that observed for unpatterned films. The improvement in edge abruptness may have resulted from the reaction and dissolution of the small particles into the substrate. Alternatively, differences in the surface free energies of the superconductor and the MgO favoring the preferential wetting of the superconductor by itself may have lead to the migration of the outstanding appendages back to the main body of material during the high temperature annealing step. A topographical view (Figure 7c) demonstrates that the edge roughness is small relative to typical device dimensions.

1394-2C

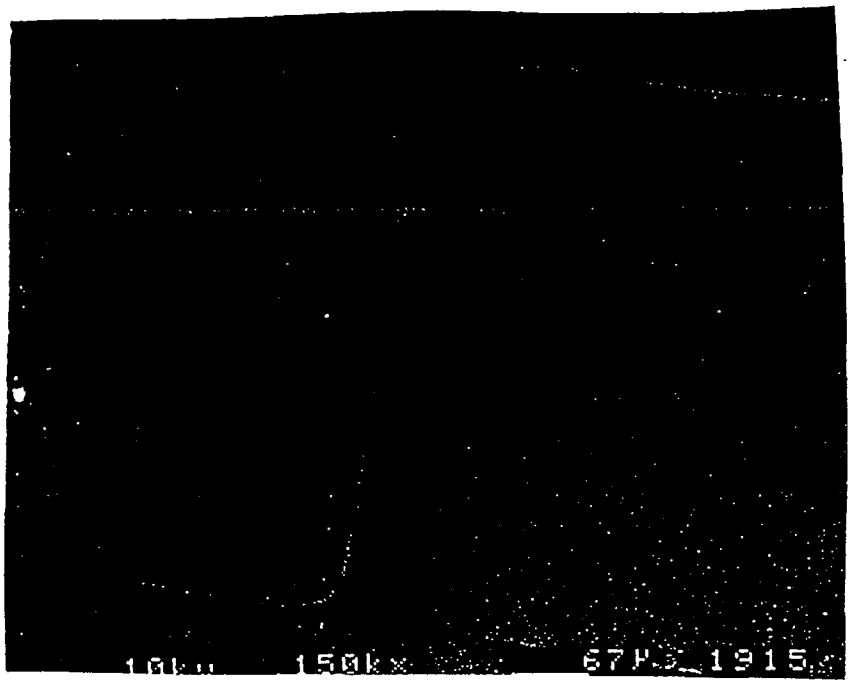
Figure 7. Fabrication of $Tl_2Ba_2CaCu_2O_x$ quarter wave resonator on MgO(100): exploded view of patterned edge in (a) BaCaCuO/MgO(100) and (b) TlBaCaCuO/ MgO(100); (c) topographical view of resonator



(a)



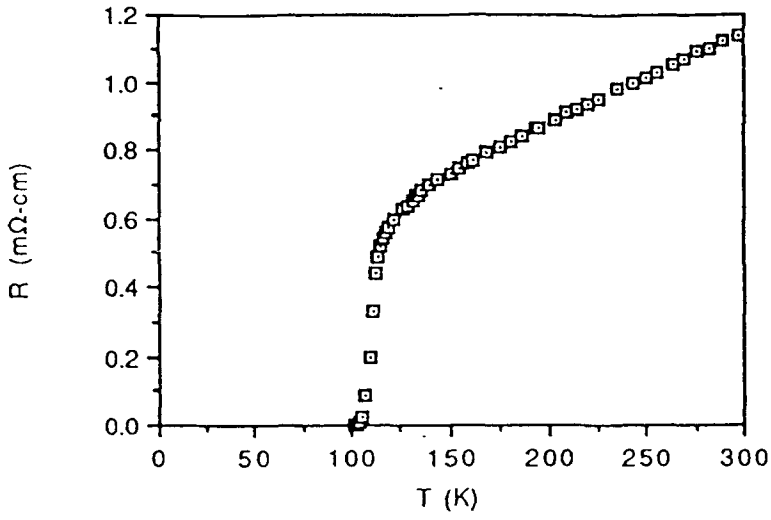
(b)



(c)

Thick , 5 to 6 μm, Al or Au ground planes for high frequency devices were deposited by sputtering or e-beam evaporation. Contact metallization with specific contact resistance less than 10^{-4} Ω/cm^2 was achieved by using a Ar ion etch prior to Ag sputter deposition followed by a rapid thermal anneal (1 min at 500°C in flowing O_2). Surface preparation is the key to obtaining low specific contact resistance on Tl-containing films because noble metals such as Ag and Au form low melting eutectics with Tl at temperatures exceeding 300°C. Consequently, standard high temperature anneals, which are effective in reducing the contact resistance on YBaCuO,[10] degrade the properties of the TlBaCaCuO/noble metal interface leading to an increase in the contact resistance. The superconducting transitions of the processed films have been measured and onsets as high as 125 K with complete transitions to superconductivity by 103 K have been observed which is essentially the same as that obtained for unpatterned films (Figure 8). A slight degradation in J_c from 10^5 to 10^4 Amps/cm^2 has been observed in 130 μm wide lines which is consistent with the increase in the normal state resistivity of the processed films. Efforts to improve the J_c values and to measure the microwave surface resistance of the patterned films are in progress.

Figure 8. Resistive transition of $Tl_2Ba_2CaCu_2O_x$ microbridge



4. CONCLUSIONS

C-axis oriented $Tl_2Ba_2CaCu_2O_x$ thin films were grown on MgO(100) by MOCVD and post annealing processes. Resistive transitions ($R \leq 0.1$ μΩ-cm) of 105 K and surface resistivities 1/2 to 1/5 that of a gold standard at 17 GHz (77 K) were obtained with unpatterned films. Thin (0.1 μm) TlBaCaCuO films functioned as bolometric detectors over a spectral range of 1.5 to 20 μm; no quantum or nonequilibrium effects were observed between 4 and 125 K. Fine features were delineated in the BaCaCuO thin films by wet chemical etching. After Tl incorporation, resistive transitions exceeding 103 K were observed in the patterned films; however, a degradation in J_c from 10^5 to 10^4 Amps/cm^2 occurred at 4 K. Current work is focused on improving the J_c and microwave surface resistance of the patterned films.

5. ACKNOWLEDGEMENTS

The authors wish to thank Eugene Venturini for the Meisnner effect data and Bob Boerstler for the microwave cavity measurements. This research was supported by DARPA under contract No. N00014-88-C-0531 and by the DOE under contract No. DE-FG05-90ER80884.

6. REFERENCES

1. R. H. Koch, W. J. Gallagher, B. Bumble, W. Y. Lee, "Low-noise thin-film TlBaCaCuO dc SQUID operated at 77 K," Appl. Phys. Lett., **54**, 951, 1989.

2. L. C. Bourne, R. B. Hammond, McD. Robinson, M. M. Eddy, W. L. Olson, T. W. James, "Low-loss microstrip delay line in $Tl_2Ba_2CaCu_2O_8$," Appl. Phys. Lett., **56**, 2333, 1990.

3. P. S. Kirlin, R. Binder, R. Gardiner, D. W. Brown, "Growth of High T_c YBaCuO thin films by metalorganic chemical vapor deposition,"Proc. SPIE: Processing of Films for High T_c Superconducting Electronics, 1187, 115, 1990.

4. N. Hamaguchi, J. Vigil, R. Gardiner, P. S. Kirlin, "Reduced Pressure MOCVD of c-Axis Oriented BiSrCaCuO Thin Films," Jpn. J. Appl. Phys., 29, L596, 1990.

5. N. Hamaguchi, R. Gardiner, P. S. Kirlin, "MOCVD of TlBaCaCuO Thin Films: Structure-Property-Processing Relationships," Appl. Surf. Sci., accepted for publication, 1990.

6. N. Hamaguchi, R. Gardiner, P. S. Kirlin, R. Dye, K. M. Hubbard, R. E. Muenchausen, "Metalorganic chemical vapor deposition of $Tl_2Ba_2CaCu_2O_x$ superconducting thin films using fluorinated ß-diketonate source reagents," Appl. Phys. Lett., accepted for publication, 1990.

7. D. G. Hamblen, "Infrared Detectors Using Bulk High T_cGranular Josephson Junctions," SDIO Final Report Contract #DASG60-88-C-0097, March 1989.

8. R. P. Vasquez, M. C. Foote, B. D. Hunt, "Reaction of nonaqueous halogen solutions with $YBa_2Cu_3O_{7-x}$," J. Appl. Phys., 66, 4866, 1989.

9. Q. X. Jia, W. A. Anderson, "Characterization of hydrofluoric acid treated Y-Ba-Cu-O oxides," J. Mater. Res., 4, 1320, 1989.

10. C. L. Huang, G. Sh. Gildenblat, S. J. Fonash, "Temperature dependence of contact resistance in noble metal/high T_c superconductor systems," J. Vac. Sci. Technol. A, 7, 3371, 1989.

ABSTRACT MRS Fall 1990 M6.3
Boston

MOCVD of TlBaCaCuO Superconducting Thin Films.
Norihito Hamaguchi, Steven A. Jones, Robin A. Gardiner, and Peter S. Kirlin, Advanced Technology Materials, Inc., 520-B Danbury Road, New Milford, CT 06776.

TlBaCaCuO films are promising for high frequency applications. We have prepared c-axis oriented TlBaCaCuO (2212 and 2223 phases) superconducting thin films by a three step process. The physical properties of the films were correlated to the high frequency properties.

BaCaCuOF precursor films were deposited on MgO (100) substrates by MOCVD using fluorinated ß-diketonates of Ba, Ca, and Cu. The post-annealing process consisted of two steps: fluorine removal and thallium incorporation. The films were first annealed in wet oxygen between 550°C and 800°C. Films annealed below 650°C retained fluorine. This residual fluorine prevented the formation of high T_c phase, although the second annealing step resulted in complete fluorine removal. Thallium was then diffused into the BaCaCuO films at temperatures between 850°C and 900°C in the presence of $Tl_2O_3/Ba_2Ca_2Cu_3O_x$ pellets.

The effect of processing conditions on the microstructure and phase purity was invesigated by SEM-EDX and X-ray diffractometry. The protocol for the second annealing step and relative configuration of the film and pellets were found to play a crucial role in the high T_c phase formation. Development of high T_c phase was observed as the annealing time was increased. The best films had surface resistivities an order of magnitude lower than gold at 17 GHz at 77K.